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Influence of the yttria content on the mechanical properties of Y_2O_3-ZrO_2 thin films prepared by EB-PVD

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Abstract

A mechanical characterization study of the whole range $(ZrO_2)_{1-x}$–$(Y_2O_3)_x$ system is presented for thin film samples. Films have been prepared by Electron Beam Physical Vapour Deposition (EB-PVD) on Si(1 0 0) substrates. The mechanical characterization, obtained from nanoindentation and Brillouin Light scattering (BLS) techniques, shows a monotonous behaviour between the two pure compounds of the series except for the film with 0.08 Y_2O_3 molar content of yttria-stabilized zirconia (YSZ) solid solution that presents an anomalous hard value. Additionally, BLS is presented as an alternative technique to the study of the mechanical properties of this system.

Keywords: EB-PVD preparation of yttria-stabilized zirconia thin films; Mechanical properties yttria zirconia system

1. Introduction

Zirconium oxide is a widely used material because of its heat resistance, low thermal conductivity, high refractive index and high transparency in the visible and near infrared region, very high chemical inertness and high laser damage threshold. Due to these properties, its applications can be found in very different aspects of technology. For instance, zirconia has been applied as thermal barrier coating (TBC) [1], optical filters, laser mirrors [2], buffer layer for high T_C superconductor on Si [3], high temperature oxygen separation [4], oxygen sensors [5], and solid oxide fuel cells [6]. For those applications, and especially for TBC, hardness and general mechanical properties are characteristics of most important relevance for durability and developing superior coatings.

Films of zirconia can be prepared by different techniques. Typically, thin films prepared by sputtering are used for gate dielectric in microelectronics applications and zirconia films prepared by electron beam physical vapour deposition (EB-PVD) are candidates for advanced TBC for the new generation of land-based gas turbines [7]. Although EB-PVD zirconia films show higher thermal conductivities, and thus smaller insulation, than plasma sprayed TBCs, they have been applied to the hot components of jet engines because of their high reliability under several thermal-cyclic environments [8].

Typically, ZrO_2 presents monoclinic and tetragonal crystallographic structures, being the tetragonal one the most suitable for common applications. The tetragonal phase of ZrO_2 is unstable at room temperature, but typically, stabilization has been obtained by doping with cations as Y^{3+} or Ca^{2+} [9]. The obtained low thermal conductivity magnitude for the films is mainly due to two factors: the film microstructure and the intrinsic thermal conductivity value. For YSZ system, this second factor is related with the oxygen defect structure which is induced when in the solid solution Zr^{4+} ions are substituted with trivalent Y^{3+} ions giving rise to oxygen vacancies to compensate electrical charge.

In this paper, we compare the mechanical properties of thin films, with different zirconia/yttria relationship,

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prepared by EB-PVD. Hardness and Young's modulus has been determined by nanoindentation and presented their comparison with the elastic constants obtained by BLS.

2. Experimental

ZrO_2 films have been prepared using a 6 kW electron beam source EVM-6 from Ferrotec GmbH, operated with a GENIUS evaporation controller with a CARRERA high voltage power supply. The source was located in a standard PLS-500 Pfeiffer chamber equipped with a secondary load-lock chamber. The vacuum system provides a residual pressure of 1×10^{-7} mbar and the typical pressure during deposition was about 1×10^{-5} mbar.

Samples were deposited at room temperature from several starting ZrO_2 materials: (i) ceramic blocks of YSZ (0.08 Y_2O_3 molar content) were prepared with some different densities by hot-pressing in order to be used as target for the electron beam gun (we will refer to these samples as *YSZ-films*); (ii) a series of sintered pellets with different Y_2O_3 concentration were prepared as starting material for film deposition by EB-PVD. This starting material was fabricated by pressing at room temperature and sintered at 1300 °C a blend of the two oxides with the required yttria content. Pellets of the $(ZrO_2)_{1-x}$–$(Y_2O_3)_x$ series have been prepared with $x = 0$, 0.04, 0.06, 0.11, 0.19, 0.3 and 1 (we will refer to the films prepared in this way as *ZrYO-films*). Main parameters in EB-PVD preparation are electron-beam acceleration voltage and the electron-beam current intensity. For this study, thin films of about 2 μm thick were prepared on non-intentionally heated Si(1 0 0) with 8 kV and 70 mA, which allow a deposition rate of 2 μm/h.

Glow discharge optical emission spectroscopy (GDOES) depth profile analysis of the films were completed using a Jobin–Yvon RF-GD Profiler operating at a typical radio frequency discharge pressure of 650 Pa and power of 40 W on a 4 mm diameter anode.

A combined use of particle induced X-ray emission (PIXE) and Rutherford backscattering spectroscopy (RBS) was employed to determine the composition and thickness of the films. The samples were analyzed with a He^+ beam at 2 MeV, with the RBS detector placed at 165° and the Si(Li) detector for PIXE situated at 145°.

Nanoindentation experiments were made with a Nanoindenter II's (MTS Systems, Oak Ridge, TN) using a Berkovich diamond tip. Each specimen was tested at room temperature using the continuous stiffness measurement technique developed by Oliver and Pethica [10]. In order to obtain hardness (or Young's modulus) the continuous stiffness measurements have been converted in a point-to-point curve by averaging every 25 nm of the tip contact displacement (that permits to have mean value and deviation for each point). A minimum of 10 indentations were made in each specimen taking as the final values for the hardness and Young's modulus the statistical mean value with its corresponding standard deviation.

The experimental set up for BLS was already described elsewhere [11]. It can be summarized as follows: The light source was a 2060 Beamlok Spectra Physics Ar^+ ion laser provided with an intracavity temperature stabilized single-mode and single-frequency z-lok etalon ($\lambda_0 = 514.5$ nm). The scattered light was analysed using a Sandercock-type 3 + 3 tandem Fabry–Pérot interferometer [12]. The typical values for finesse and contrast were 150 and 10^9, respectively. As far as the films are deposited on opaque substrates only the backscattering geometry (1 8 0) can be applied with the scattering wave vector off-plane. The zirconia films are transparent thus allowing the existence of a supplementary scattering geometry ($2\alpha A$) with the wave vector in-plane due to the reflection of the incident laser beam on the substrate as has been shown in [13,14]. The sound propagation velocity (V_S) of the film is thus: $V_S = f^{180}\lambda_0/2n$, or $V_S = f^{2\alpha A}\lambda_0/2\,\sin(\alpha)$, where f^{180} and $f^{2\alpha A}$ are the Brillouin frequency shifts for backscattering and supplementary scattering geometries, λ_0 is the laser wavelength, n the refractive index of the film and α the angle between film normal and laser beam. In the case of elastic isotropic media, the combination of both scattering geometries also delivers the information about n.

3. Results and discussion

When making zirconia with different yttria content, the first question that should be answered is how much the yttria concentration is in the thin film. Energy dispersive spectroscopy installed on a scanning electron microscope does not give reliable results because of the superposition of yttrium and zirconium emission lines. Alternatively, GDOES can be used for depth profiling of nanometric layer systems since it combines the ability to provide the atomic composition of the layers with a high depth resolution. GDOES results show depth homogeneity in films and porosity that increases with yttria content.

Fig. 1 shows the RBS spectra of some selected samples as well as their simulation performed by the "SIMRA" software. Spectra shows the O and Zr/Y contributions as well as a small Hf amount due to impurities in the ZrO_2 starting powder. It is apparent from this figure that the mass resolution is not good enough to discriminate between the signals from yttrium and zirconium. However, the relative concentration of these two elements has been determined from the PIXE spectra, where the K lines from Y and Zr are completely separated. The area of the K_α peaks was obtained using the AXIL code and corrected with the corresponding cross sections for Zr and Y ($\sigma_{Zr}/\sigma_Y = 1.34$). From the RBS and PIXE results we can affirm that the film's composition correspond to that contained in the starting material, which allows the conclusion that no compositional change takes place during the thin film preparation by EB-PVD.

Fig. 2 shows, as a matter of example, the results for the hardness and Young's modulus obtained as a function of the indenter tip contact displacement for a *YSZ-film*

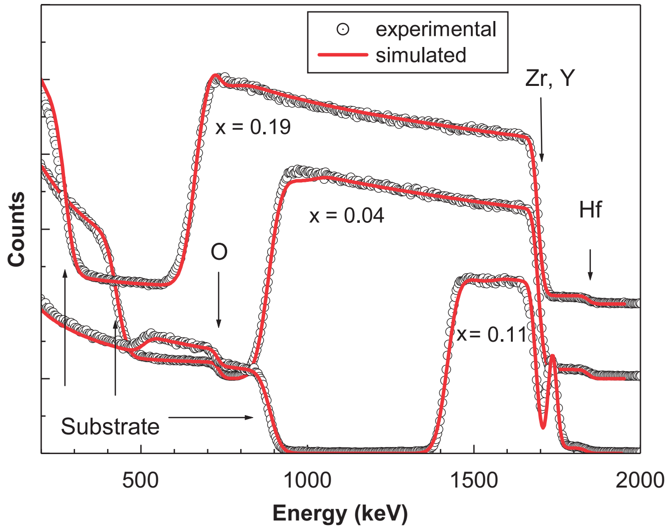

Fig. 1. Experimental RBS data and simulation for three selected samples. The corresponding yttria molar content is given in the picture as x in the formula $(ZrO_2)_{1-x}$–$(Y_2O_3)_x$. The $x = 0.11$ spectrum shows a small contribution of silver at the surface that is not a part of the deposited film.

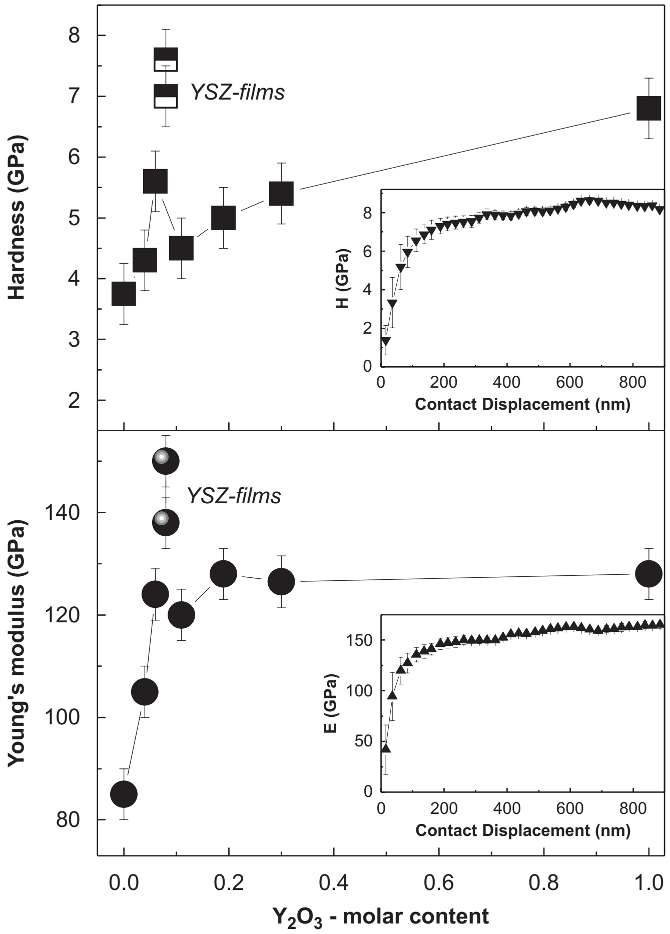

Fig. 2. Hardness and Young's modulus measurements obtained for a *YSZ-film*. The inset shows the behaviour of H and E vs. the yttria molar content in the film.

(grown from the YSZ target). The continuous stiffness measurement technique is very useful in determining the mechanical properties of thin films because it allows the study of mechanical properties evolution of samples continuously as the indenter displacement is increased [15]. In this way, the substrate effect can be detected in an easier way than with the traditional nanoindentation experiment. Results show hardness and Young's modulus values almost constant with the tip contact displacement and different from those of the silicon used as a substrate. This indicates that the obtained hardness values correspond to the film unaffected by the silicon substrate. Usually, it is considered that if the indentation depth is smaller than 10% of the film thickness, the substrate has no effect in the film hardness determination [10]. As the film thickness is 2–4 μm, we can obtain the hardness values for our samples with no effect from the silicon. Otherwise, measurement of the Young's modulus is affected by the substrate no matter how shallow are the indentations done.

The yttria concentrations obtained after RBS and PIXE experiments permit to draw the hardness and Young modulus dependence shown in Fig. 2. The obtained values for the *YSZ-films* are slightly lower than those reported by other authors [16,17] in samples deposited under different conditions. A possible explanation could be found in the presence of a small amount of an amorphous phase in the films that, having smaller elastic constants, would diminish the film hardness and elastic modulus. Additionally, there are two other interesting facts: first, *YSZ-films* present higher hardness and Young modulus values than the whole *ZrYO-films* series; and second, *ZrYO-films* present a dependence of the mechanical properties vs. the yttrium content. The anomalous high values of *YSZ-films* respect to the pure ZrO_2 and Y_2O_3 compounds should be explained because, as in the starting material, these films are formed by a solid solution of both components that confers a particular arrangement of the oxygen vacancies, due to the substitution of Zr^{4+} by Y^{3+} cations, which has a direct effect on the films mechanical properties. A similar example can be found in $LiNbO_3$ singlecrystals with different stoichiometries [18]. On the other hand, *ZrYO-films* behave as ZrO_2 and Y_2O_3 mixtures formed by more or less independent grains that allow mechanical properties going monotonically between both pure values. Film with $x = 0.06$, which has the closest concentration to the *YSZ-films,* presents an anomalous higher value of hardness (and also of elastic modulus), it can be explained by considering a solid solution structural phase with an arrangement of oxygen defect, which is only possible to obtain in the nearness of 0.08 Y_2O_3 molar content.

Fig. 3 shows a typical *YSZ-film* BLS spectrum and the evolution of the obtained elastic constant C_{11} with the yttria content in the *ZrYO-films* series. As has been described above, from the position of the BLS peaks it is straightforward to determine the sound propagation velocity in the film [14]. The relationship between sound

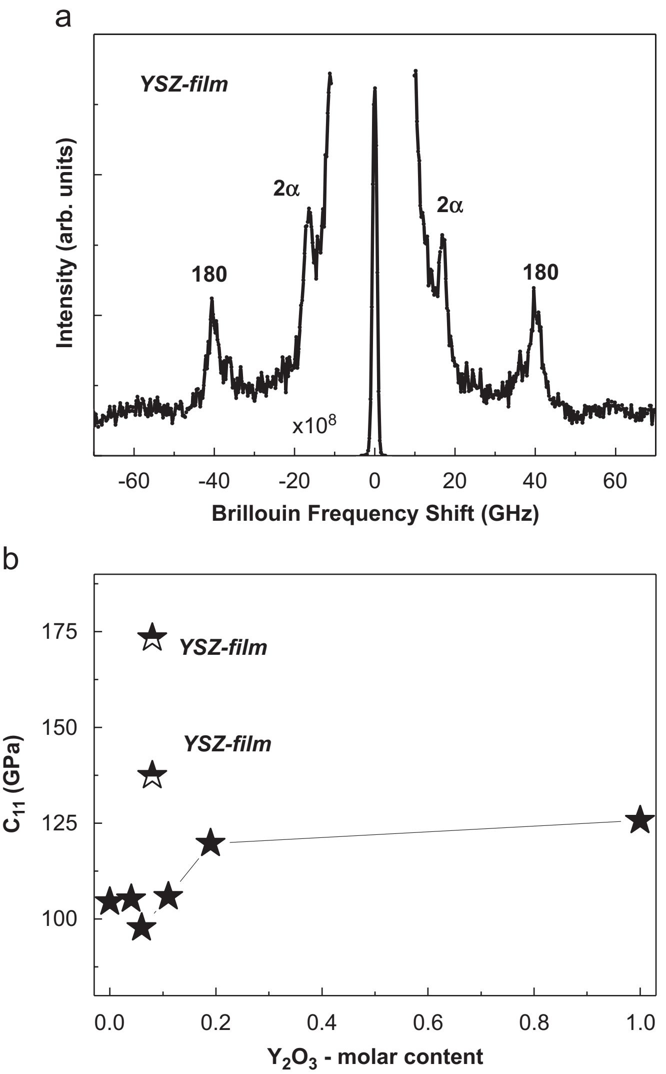

Fig. 3. (a) Brillouin spectrum of a *YSZ-film*, the backscattering (1 8 0) and quasi-90° ($2\alpha A$) geometries can be observed. (b) Dependence of the C_{11} elastic constant obtained from Brillouin scattering data vs. the yttria molar content in the film.

velocity and elastic constants is density mediated: $C_{11} = \rho V_S^2$. Obviously, it is necessary to have information about the density of the studied material in order to assess the evolution of the elastic constant. In isotropic media there exists a well-established relationship between density and refractive index known as Lorentz-Lorentz relation [19]. In the case of the *ZrYO-films*, the density was calculated by interpolation between the pure ZrO_2 and Y_2O_3 corresponding values [20]. The BLS refractive index for pure Y_2O_3 film is in agreement with that reported in the literature ($n = 1.79$) [20] while the value obtained for pure ZrO_2 film is extremely low (1.73) when compared with its usual value of 2.2 [20]. This fact indicates that also the density of the ZrO_2 film has to be lower than the expected one. Using the Lorentz-Lorentz relation, it is possible to estimate the film density to be 4.337 g/cm^3. This is the value used for the calculation of the corresponding elastic constant. The BLS-obtained elastic constant values show the same behaviour as the nanoindentation Young's modulus; furthermore, the absolute values are clearly lower than the single-crystal corresponding ones [21–23]. The BLS results confirm the considerations made by taking into account the nanoindentation technique.

4. Conclusions

ZrO_2 films have been prepared by EB-PVD technique from different starting materials. Its mechanical properties have been determined by nanoindentation and BLS scattering spectroscopy; both techniques show their complementarities in the elastic characterization of thin film and allow to conclude that, *YSZ-films* prepared from YSZ (0.08 Y_2O_3 molar content) at room temperature present higher hardness and Young modulus values than the whole *ZrYO-films* series prepared from Y_2O_3–ZrO_2 mixtures at room temperature. This fact can be explained because *YSZ-films* are formed by a solid solution that confers a defined arrangement of oxygen vacancies in the crystallographic lattice, due to the substitution of Zr^{4+} by Y^{3+} cations, having a direct effect on the films elastic properties. *ZrYO-films* present a dependence of the mechanical properties vs. the yttria content. This series behaves as composed by two independent phases formed by ZrO_2 and Y_2O_3 grains, respectively. The obtained mechanical behaviour fits to a monotonical increase between two values corresponding to the pure concentrations. However, near to 0.08 Y_2O_3 molar content, films present anomalous higher values of hardness and elastic modulus. This anomaly can be explained by taking into account the formation of a solid solution, similar to the YSZ structural phase, which would be obtained at the film without any additional thermal treatment.

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